324. *Some Uses of Dielectric Polarisations in the Investigation of the Formation of Intermolecular Complexes in Solution.*

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The method recently employed by Earp and Glasstone for the determination of association constants and dipole moments of complexes between donor and acceptor molecules, by measuring the dielectric polarisations of binary mixtures, has been investigated further. Modifications of the method have been suggested and examined, and it has been concluded that measurements of this kind alone cannot be expected to give conclusive results. To do this, it seems that the measurements must be combined with independent measurements of the equilibrium constant, and possible methods have been indicated.

The existence of intermolecular " complexes " in the liquid phases of binary mixtures of organic substances has often been inferred from the non-additive nature of the physical properties of such mixtures. In the absence of confirmation by independent evidence, such inferences are always suspect, owing to the great difficulty in deciding whether the observed abnormality is due to chemical interaction or to forces of a " van der Waals " character. Dipole moments are, however, but little affected by the ordinary van der Waals cohesion, and it is for this reason that the recent work of Earp and Glasstone (J., 1935, 1709, 1720; cf. Glasstone, *Trans. Faraday Soc.*, 1937, **33**, 200) is of special interest. As we propose to criticise their interpretation of their results, we give in outline the method they used for determining the extent of the association, and the polarisation of the complex.

From the measurements of the dielectric constant and the density of their binary mixtures, they calculate the dielectric polarisation by means of the Debye equation

$$P = M(\varepsilon - 1)/d(\varepsilon + 2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In their view, it is a consequence of the law of mass action that, if a compound is formed between two substances, then, when one of these is in large excess, the other exists entirely in the form of compound. Using this conception, they derive values of the constant and polarisation of the compound thus: Let two liquids, A and B, be mixed in molar fractions a and b, of which amounts $\Delta a = \Delta b = x$ go over into the form of the 1 : 1-compound AB = X. Then the total polarisation, P, of (1) is written in the form

$$P = P_A(a - x)/(1 - x) + P_B(b - x)/(1 - x) + P_X x/(1 - x) \quad . \quad . \quad (2)$$

where P_X is the polarisation of the compound. If P_A, the polarisation of A in the mixture, is the same as that in pure liquid A at all compositions, then Q_B, the apparent polarisation of B on the assumption that there is no compound formation, can be obtained from the simple mixture law

$$P = P_A a + Q_B b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

When the values of Q_B obtained in this way are plotted against b, they give a falling curve, having its highest value when $b = 0$. But this value is, by hypothesis, due entirely to compound, and Earp and Glasstone derive the actual polarisation, P_X, of this from the equation

$$P_X = (Q_B)_{b=0} + P_A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)^*$$

This value of P_X can be substituted in (2), and this can be solved for x. The value of x is inserted in the mass-action expression

$$K = x(1 - x)/(a - x)(b - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which assumes that molar fractions may be treated as active masses. The values of P_A and P_B substituted in (2) are corrected for dielectric-constant effect by measurements on A and B separately in inert solvents, and P_X is corrected approximately by finding its value

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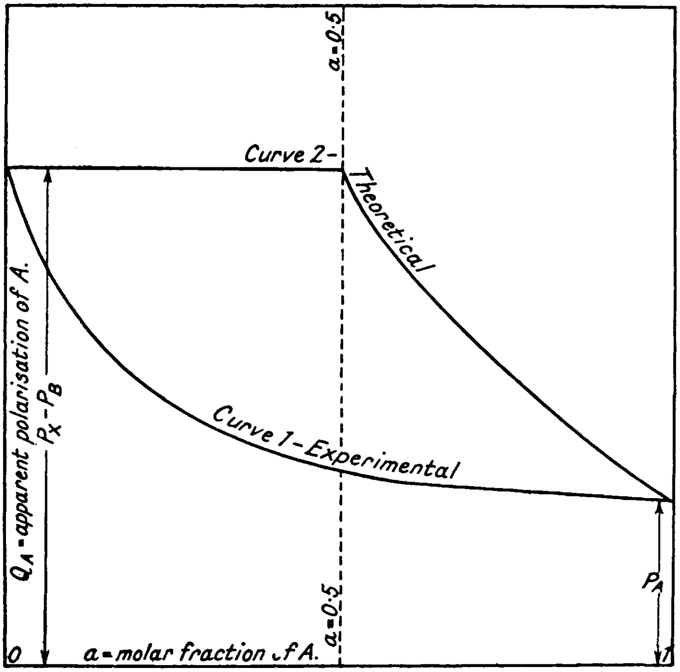
* We are unable to derive this equation from (2); it can, however, be obtained from (7), assuming with Earp and Glasstone that all the solute is in the form of compound at infinite dilution.

at points $a = 0$ and $b = 0$, and interpolating along the straight line joining the two. If these values are nearly alike, it is taken to indicate the correctness of the method, whereas, if they differ largely, the difference is attributed to natural variation with the dielectric constant of the medium.

We are unable to agree with this theory of the method, however, on the following points :

(I) *At infinite dilution of A in B, all the A is in the form of AB.* If the reaction is A + B = AB, then, from (5), it is clear that $f_{AB}/f_A = Kf_B$, which can never be infinite unless K itself is infinite, since f_B can never be greater than 1. And if K were infinite, the curve for Q_A would not follow the experimental form (Curve 1), but would have the form of Curve 2.



If K is infinite, then, so long as $a < 0{\cdot}5$, A is all in the form of AB and so, dielectric-constant effects being neglected, its apparent polarisation is constant. When $a > 0{\cdot}5$, eq. (7) (below) reduces to the form

$$P = (2a - 1)P_A + (1 - a)P_X$$

and if this is combined with an equation of the form (3)

$$P = aQ_A + bP_B = aQ_A + (1 - a)P_B,$$

Q_A is given by

$$Q_A = 2P_A + P_B - P_X + (P_X - P_A - P_B)/a$$

which diminishes as a increases to the limiting value P_A when $a = 1$. This is shown in Curve 2. Curve 1 is the kind of curve obtained (usually) experimentally.

(II) Equation (2) certainly represents the relationship between P, P_A, P_B, and P_X if P is calculated from the *true* mean molecular weight, compound formation being taken into account, but Earp and Glasstone use the ordinary value of P, calculated from $M = aM_A + bM_B$. The true value is $M_O = (aM_A + bM_B)/(1 - x)$, so that, if P_O is the true polarisation of the mixture, *i.e.*, $P_O = (\varepsilon - 1)M_O/d(\varepsilon + 2)$ (equation 1), and P is the value obtained when the compound formation is neglected [see (1)], it is clear that

$$P = P_O(1 - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

With this significance of P, therefore, equation (2) must be rewritten in the form

$$P = P_A(a - x) + P_B(b - x) + P_Xx \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

(III) It is very doubtful whether the law of mass action can be applied over a 100% range of binary mixtures, an application which is not at all analogous to the use of the law when one of the reactants is present in large and *constant* concentration.

We feel therefore that this method cannot safely be applied. Alternative methods for the solution of the problem have been attempted during the course of the present work and are outlined below.

Method 1. *Successive Approximation.*—This was carried out in the following stages: (*a*) Assume, with Earp and Glasstone, that all the solute at infinite dilution has combined to give the complex and so calculate P_X, the polarisation of the complex, from (4); (*b*) substitute this value in (7), and obtain a value for x; (*c*) insert this value of x in (5) and calculate K; (*d*) use this to calculate the amount of compound present at infinite dilution, and then obtain a new value for P_X. Then repeat these stages until it is possible to extrapolate to the true values. An attempt was made to apply this method to the ethyl ether–chloroform data of Earp and Glasstone (*loc. cit.*), but the convergence of the results was so slow that extrapolation was impossible.

Method 2.—If Q_A is the apparent polarisation of A at infinite dilution in B, calculated by assuming that the polarisation of B is the same as that in its pure liquid form, it is easy to show that its true value is given by

$$K = (Q_A - P_A)/(P_X - P_B - Q_A) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Similarly for B at infinite dilution in A

$$K = (Q_B - P_B)/(P_X - P_A - Q_B)^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

K can be eliminated from these to give an equation in which the only unknown is P_X:

$$(Q_A - P_A)(P_X - P_A - Q_B) = (Q_B - P_B)(P_X - P_B - Q_A) \quad . \quad . \quad (10)$$

But it is here assumed (*a*) that K holds constant over the whole range, an assumption which has already been questioned, and (*b*) that P_X has the same value over the whole range, which is certainly untrue. It is not possible to remedy (*a*), but a tentative allowance can be made for (*b*) by assuming that the variation in the polarisation of the compound is the sum of those of its two constituents, which are known. It is unfortunate that the accuracy of this correction is very important when P_X is nearly the same as $P_A + Q_B$ or $P_B + Q_A$, where also it is necessary to extrapolate accurately the values of Q_A and Q_B. Since this cannot be done, and in view of the other assumptions, it is not surprising that no reliable results were obtained by this method when applied to the following data:

Diethyl ether and chloroform at 20° (Earp and Glasstone):

$A = Et_2O$, $B = CHCl_3$.
$Q_A = 90$ c.c., P_A (in ether) = 55, (in chloroform) = 54.
$Q_B = 75$ c.c., P_B (in ether) = 46, (in chloroform) = 45.

Diethyl ether and chloroform at 0° (Tables I and II):

$Q_A = 92$ c.c., P_A (in ether) = 55·8, (in chloroform) = 55·4.
$Q_B = 78$ c.c., P_B (in ether) = 46·4, (in chloroform) = 45·5.

Diïsopropyl ether and chloroform at 25° (Tables III and IV).

Diïsopropyl ether and chloroform at 0° (Tables V and VI).

Each of these systems gives absurd results, with values of P_X less than $P_B + Q_A$, or $P_A + Q_B$, and consequently negative values for K.

Method 3.—This was an attempt to dispense with the assumption that K is constant over a range of 100%, by making measurements at two different temperatures, and assuming

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* In the expression, $Q_A - P_A$, P_A is the value of the polarisation of A at the dielectric constant of pure B, in which Q_A is measured. This is obtained by measurements in an inert solvent. In the expression $P_X - P_B - Q_A$, P_B is the value at the same point, *i.e.*, in pure liquid B. To introduce specific symbols for these would have made the equations too cumbrous, and the context makes clear what is required.

that the ratio K (first temp.)/K(second temp.) was the same at both ends of the composition scale. This merely requires that the heats of combination of the two constituents shall be the same whatever the composition. If equations (8) and (9) are rewritten with values of polarisations corresponding to another temperature, *i.e.*,

$$K' = (Q'_A - P'_A)/(P'_X - P'_B - Q'_A) \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$K' = (Q'_B - P'_B)/(P'_X - P'_A - Q'_B) \quad . \quad . \quad . \quad . \quad . \quad (12)$$

then (9) can be divided by (12) and (8) by (11), and the ratio K/K' eliminated between the two resultant equations. The final equation is

$$(Q_A - P_A)(Q'_B - P'_B)(P_X - P_A - Q_B)(P'_X - P'_B - Q'_A)$$
$$= (Q_B - P_B)(Q'_A - P'_A)(P_X - P_B - Q_A)(P'_X - P'_A - Q'_B) \quad . \quad . \quad (13)$$

There are still two unknowns in this equation, P_X and P'_X, but one of these can be eliminated by writing them in the form, $P = P_E + P_O$, of which P_E is independent of the temperature, and can be evaluated (as Earp and Glasstone have shown) from the electron polarisations of the two constituents. P_O is inversely proportional to the temperature, so that $P'_O = TP_O/T'$. Measurements have been made on the di*iso*propyl ether–chloroform system at 0° and 25° (*vide supra* and Tables III—VI), and by taking the values worked out above in Method 2, the following equation was obtained for P_O :

$$9{\cdot}676\ P_O^2 - 1905{\cdot}4\ P_O + 77379 = 0$$

The solution of this gives $P_O = 139{\cdot}6$ or $99{\cdot}9$, of which the latter is impossible since it gives a negative value of K. Taking the former, we have :

$$P_X\ (0°) = P_O + P_E = 139{\cdot}6 + 52{\cdot}3 = 191{\cdot}9 \text{ c.c.}$$

$$P'_X\ (25°) = P'_O + P_E = 127{\cdot}9 + 52{\cdot}3 = 180{\cdot}2 \text{ c.c.}$$

These values can be used to obtain values for K at both ends of the scale at the two temperatures, and hence the value of the heat of combination. The results are:

K for dilute solutions of di*iso*propyl ether in chloroform, at 0° = 1·13, at 25° = 1·33;
K for dilute solutions of chloroform in di*iso*propyl ether, at 0° = 3·08, at 25° = 3·68,

from which it is clear that no reliance can be placed on the absolute values of the results, for K apparently increases with the temperature. This would require the reaction to be endothermic, whereas the results of McLeod and Wilson (*Trans. Faraday Soc.*, 1935, **31**, 596) show that such reactions are exothermic; in fact, the heat of reaction could be felt when the components of this system, and particularly of the chloroform–triethylamine system, were mixed. It is possible, however, that the method would be applicable if a wider temperature range were used, and preliminary experiments have been made with a view to conducting measurements at − 45° and + 25°.

Method 4.—This also was an attempt to dispense with the assumption that K is constant over the whole range, by making measurements (*a*) on a dilute solution of A in B, and (*b*) on a dilute solution of A in a constant-ratio mixture of B and an inert solvent, such as benzene. By methods similar to those of Method 2 it was possible to deduce the equation

$$(Q_A - P_A)(P_X - P_B - Q_{Am}) = (Q_{Am} - P_A)(P_X - P_B - Q_A)b \quad . \quad . \quad (14)$$

where b is the molar fraction of B in the constant-ratio mixture, and Q_{Am} is the apparent polarisation of A at infinite dilution in the mixture. The results with which this method was tested are in Tables III, IV, VII, and VIII, for the chloroform–di*iso*propyl ether system, and the following figures are drawn from these :

*Dilute chloroform in a di*iso*propyl ether–benzene mixture at* 25° :

$Q_A - P_A = 53$, $Q_{Am} - P_A = 46$, $Q_A + P_B = 167$, $Q_{Am} + P_B = 161$ c.c.; $b = 0{\cdot}7899$.
Results : $P_X = 227$ c.c., $K = 0{\cdot}88$.

This result is different, though not impossibly different in view of the difficulties of the method and the enormous probable error, from that of the previous method (for chloroform in di*iso*propyl ether), but any confidence in its value is shaken when the result is compared with the corresponding one for dilute solutions of the ether in chloroform (P_X = *ca.* 180 c.c.).

Method 5.—It is now considered that only the following modification of the dielectric-constant method can produce significant results. It is virtually an abandonment altogether of the use of binary liquid mixtures, and a reversion to measurements of dilute solutions of the two components in a third, unreactive, solvent (Hassel and Uhl, *Z. physikal. Chem.*, 1930, *B*, 8, 187; Laurent, *Compt. rend.*, 1934, **199**, 582; 1935, **201**, 554). Comparisons of the polarisation values obtained in this way with those to be expected if no compound were formed (corrected for dielectric constant effect) show a linear increase of the observed values with concentration, if the two reactive components are present in constant proportion. It is easily shown * that, if R is the difference between the observed value of polarisation of a mixture and the theoretical value for no compound formation then

$$R = (P_X - P_A - P_B)x/(a + b) \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Thus, either P_X or x can be evaluated if the other is known, whereas, if neither is known, the function $(P_X - P_A - P_B)x$ can be used to give comparative data for various systems, on the probable assumption that the compound with the greatest polarisation-increase has also the greatest stability. Measurements have been made in this way on the systems chloroform–di*iso*propyl ether, chloroform–triethylamine, and chloroform–nitromethane, and the results are contained in Tables IX—XI. In these, Q (col. 5) is the observed polarisation of the mixture, while P_O (col. 6) is the calculated value on the assumption that no compound is formed, and R (col. 7) is the difference $Q - P_O$. The value of R is considerable for chloroform–triethylamine, noticeable for chloroform–di*iso*propyl ether, and within experimental uncertainty (due to the large dielectric-constant effect of the solvent) for chloroform–nitromethane; therefore, it seems that triethylamine forms the complex most readily, di*iso*propyl ether less readily, and nitromethane not at all.

This result, as far as it goes, is in accordance with what we should expect if, as Earp and Glasstone suggest, the compounds are the result of the formation of a hydrogen bond between the donor atom of the amine or ether and a hydrogen of the chloroform. It is well known that amines have more pronounced donor properties than the ethers, forming, for example, ammonium salts much more readily than the latter form oxonium salts, while nitro-compounds do not act as bases at all.

Merely to use polarisation measurements to obtain a qualitative estimate of the degree of complex formation is not, however, to make the best use of them. But it has been shown that it is in practice very difficult to derive an exact measure of both the polarisation and the degree of association from these measurements alone, and so future developments must probably use these in conjunction with independent methods of determining the degree of association. Such methods are cryoscopic and partition measurements.

EXPERIMENTAL.

The dielectric constants were measured by the heterodyne beat method (Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668), and the densities in an Ostwald–Sprengel pyknometer. Benzene ("AnalaR") was purified by freezing 2½ l. out three times, and rejecting each time the first 150 c.c. of the melt to remove homologues. It was distilled as required in a stream of dry air, after refluxing over phosphoric oxide for an hour. Chloroform ("AnalaR") was washed four times with concentrated sulphuric acid, then with N-sodium hydroxide and water, dried overnight over calcium chloride in dark bottles, refluxed over phosphoric oxide, and distilled in dry air as required. No specimen was kept for more than 2 days without repurification. Diethyl ether was washed with sodium hydroxide solution and water, dried over calcium chloride and

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* Let the molar fractions of A, B, and inert solvent be a, b, and h, if compound formation is neglected. Then, if a compound is formed, the molar fractions of A, B, AB, and solvent become $(a - x)/(1 - x)$, $(b - x)/(1 - x)$, $x/(1 - x)$, and $h/(1 - x)$ respectively. The total polarisation is

$$P_T = P_A(a - x) + P_B(b - x) + P_X x + P_H h \text{ (cf. equation 8)}$$

From the mixture law, the polarisation of the mixture of A, B, and AB is $(P_T - P_H h)/(a + b)$

or, $$Q = [P_A(a - x) + P_B(b - x) + P_X x]/(a + b)$$

By a similar calculation, if no compound were formed at all,

$$P = (P_A a + P_B b)/(a + b)$$

so that $$Q - P = R = (P_X - P_A - P_B)x/(a + b).$$

over sodium, and distilled from sodium in dry air as required. Di*iso*propyl ether was shaken with potassium permanganate until the colour was no longer discharged (to remove the explosive peroxide) and then treated in the same way as diethyl ether. Triethylamine was dried over potassium hydroxide, from which it was distilled in dry air as required. Its solutions were placed in a desiccator immediately after preparation, as the amine is very hygroscopic. Nitromethane was refluxed for several hours in dry air until the smell of hydrogen cyanide was very faint. It was then allowed to stand over calcium chloride, and was distilled from phosphoric oxide through a plug of glass wool as required.

Results.—In the tables, f_2 = molar fraction of solute; ε = dielectric constant; d = density; P = total polarisation, Q_2 = apparent polarisation of solute when that of solvent is taken to be the same as in the pure liquid.

TABLE I.

Dilute Chloroform in Diethyl Ether at 0°.

f_2.	ϵ.	d.	P.	Q_2.
0·00000	4·7110	0·7342	55·794	—
0·02247	4·8303	0·7491	56·220	74·8
0·04290	4·9370	0·7632	56·531	73·0
0·05744	4·9989	0·7725	56·715	71·8
0·08626	5·1261	0·7919	57·046	70·3

TABLE II.

Dilute Diethyl Ether in Chloroform at 0°.

f_2.	ϵ.	d.	P.	Q_2.
0·00000	5·1608	1·5230	45·549	—
0·01420	5·2651	1·5093	46·190	90·7
0·01424	5·2616	1·5091	46·177	89·7
0·03535	5·3929	1·4887	47·015	87·1
0·05806	5·5183	1·4659	47·868	85·5
0·09392	5·7727	1·4340	49·122	83·6

TABLE III.

*Dilute Chloroform in Di*iso*propyl Ether at 25°.*

0·00000	3·8658	0·7194	69·345	—
0·01974	3·9511	0·7276	69·824	93·6
0·05386	4·0126	0·7346	70·048	90·1
0·08569	4·2380	0·7604	70·714	85·3
0·12304	4·4006	0·7791	71·083	83·5

TABLE IV.

*Dilute Di*iso*propyl Ether in Chloroform at 25°.*

0·00000	4·7250	1·4812	44·647	—
0·01127	4·7910	1·4676	45·537	105·9
0·02264	4·8428	1·4534	45·981	103·6
0·03600	4·9380	1·4373	46·903	107·3

TABLE V.

*Dilute Chloroform in Di*iso*propyl Ether at 0°.*

0·00000	4·3303	0·7437	72·232	—
0·04239	4·5765	0·7648	73·127	93·3
0·06578	4·7086	0·7770	73·459	90·7
0·14239	5·1451	0·8171	74·244	86·4

TABLE VI.

*Dilute Di*iso*propyl Ether in Chloroform at 0°.*

0·00000	5·1608	1·5230	45·549	—
0·02094	5·3281	1·4980	46·930	111·5
0·03224	5·4169	1·4841	47·682	111·7
0·06666	5·6744	1·4418	49·951	111·6

TABLE VII.

*Dilute Chloroform in a Mixture of Di*iso*propyl Ether* (78·99%) *and Benzene at* 25°.

0·00000	3·5529	0·7430	60·057	—
0·01110	3·5994	0·7482	60·377	88·9
0·02293	3·6489	0·7544	60·648	85·8
0·04201	3·7241	0·7636	61·077	84·3
0·06751	3·8196	0·7764	61·511	81·6

TABLE VIII.

*Dilute Di*iso*propyl Ether in a Mixture of Chloroform* (77·67%) *and Benzene at* 25°.

0·00000	3·9365	1·3331	40·875	—
0·01116	3·9948	1·3277	41·572	103·3
0·02305	4·0582	1·3113	42·334	104·2
0·03255	4·1106	1·3015	42·985	105·7
0·04367	4·1678	1·2917	43·662	104·7

TABLE IX.

Dilute Solution of a Mixture of Chloroform (37·54%) *and Di*iso*propyl Ether in Benzene at* 25°.

(f_2 is the molar fraction of mixture, calculated from its mean molecular weight, and Q_2 is the corresponding polarisation; P_O is the calculated polarisation on the assumption that no compound is formed, and R is the difference, $Q_2 - P_O$.)

f_2.	ϵ.	d.	P.	Q_2.	P_O.	R.
0·00000	2·2727	0·8740	26·601	—	—	—
0·02410	2·3189	0·8757	27·477	62·95	63·0	0·0
0·05844	2·3903	0·8783	28·787	64·01	62·6	1·4
0·10688	2·4950	0·8825	30·679	64·75	62·2	2·55
0·14871	2·5916	0·8843	32·373	65·42	61·9	3·5
0·16895	2·6389	0·8857	33·191	65·61	61·6	4·0

TABLE X.

Dilute Solution of a Mixture of Chloroform (47·17%) *and Triethylamine in Benzene at* 25°.*

0·00000	2·2727	0·8743	26·591	—	—	—
0·02353	2·2999	0·8770	27·160	50·79	48·8	2·0
0·05020	2·3324	0·8799	27·829	51·25	48·5	2·75
0·09970	2·4010	0·8858	29·177	52·53	47·8	4·7
0·18645	2·5413	0·8956	31·791	54·48	47·0	7·5

TABLE XI.

Dilute Solution of a Mixture of Chloroform (35·72%) *and Nitromethane in Benzene at* 25°.

0·00000	2·2727	0·8742	26·594	—	—	—
0·05188	2·7720	0·8896	32·662	143·56	143·4	0·1
0·10583	3·3140	0·9044	37·775	132·24	131·0	1·2
0·14676	3·8490	0·9220	41·531	128·46	120·2	8·2
0·24726	5·0959	0·9559	47·702	111·96	106·2	5·8

TABLE XII.

Polarisation of Chloroform in Chloroform–Benzene Mixtures at 25°.

(f_2 = molar fraction in chloroform, and P_2 its polarisation.)

f_2.	ϵ.	*d*.	*P*.	P_2.
0·00000	2·2727	0·8742	26·594	—
0·01830	2·6105	0·9766	30·671	48·48
0·34596	2·9148	1·0678	33·871	47·60
0·45986	3·1697	1·1406	35·714	46·42
0·75505	3·8940	1·3235	40·535	45·06
1·00000	4·7250	1·4812	44·647	44·65

TABLE XIII.

*Polarisation of Di*iso*propyl Ether in Di*iso*propyl Ether–Benzene Mixtures at* 25°.

f_2.	ϵ.	*d*.	*P*.	P_2.
0·00000	2·2727	0·8742	26·594	—
0·07071	2·4101	0·8574	29·741	71·09
0·12044	2·5102	0·8464	32·024	71·68
0·14055	2·5402	0·8420	32·808	70·81
0·20610	2·6578	0·8307	35·566	70·13
0·27285	2·7645	0·8182	38·297	69·49
0·44637	3·0487	0·7909	45·556	69·07
0·51687	3·1423	0·7804	48·307	68·60
0·66747	3·3666	0·7598	54·621	68·58
1·00000	3·8672	0·7194	69·114	69·11

TABLE XIV.

Polarisation of Triethylamine in Triethylamine–Benzene Mixtures at 25°.

0·00000	2·2727	0·8741	26·597	—
0·08692	2·2939	0·8585	27·954	46·53
0·22058	2·3317	0·8288	30·839	45·89
0·32388	2·3497	0·8101	32·758	45·66
0·74884	2·4000	0·7507	40·404	45·03
1·00000	2·4191	0·7248	44·805	44·80

TABLE XV.

Polarisation of Nitromethane in Nitromethane–Benzene Mixtures at 25°.

0·00000	2·2727	0·8742	26·594	—
0·06563	3·1866	0·8847	36·659	179·96
0·13509	4·2356	0·8961	43·866	154·45
0·14406	4·3718	0·8974	44·581	151·46
0·16842	4·7763	0·9017	46·465	144·58
0·16901	4·7906	0·9020	46·522	144·51

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